

Dioxygen Affinities and Biomimetic Catalytic Oxidation Performance of Transition-metal Complexes with Unsymmetrical Bis-Schiff Bases

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Abstract: The oxygenation constants and thermodynamic parameter (ΔH° , ΔS°) of Co (II) complexes with unsymmetrical bis-Schiff bases were measured and their Mn(III) complexes as models of mimicking monooxygenase were employed to catalyze epoxidation of styrene. The effect of substituent R in a salicylidene of $ML^1 \sim ML^4$ [M = Co (II), Mn (III)Cl] on the dioxygen affinities and biomimetic catalytic oxidation performance were also investigated. Among them, the MnL^4Cl containing a pendant benzoaza crown ether ring showed highest conversion and selectivity up to 54.9% and 96.9% respectively.

Keywords: Unsymmetrical bis-Schiff bases, benzoaza crown ether, transition-metal complexes, dioxygen affinities, catalytic epoxidation.

Bis-Schiff base complexes as mimetic monooxygenase have been extensively reported^{1,2}. The bis-Schiff bases transition-metal complexes modified by crown ethers ring or pseudo-macrocyclic polyethers have significantly improved dioxygen affinities and biomimetic catalytic performance in comparison with uncrowned analogues^{3,4}. However, most of them were symmetric and oxacrown ether substituted, the bis-Schiff bases bearing an azacrown ether, with special configuration and possibility to approach the coordination center⁵, have not been reported yet. In order to discover the influence of the bonded azacrown ether on the dioxygen affinities and biomimetic catalytic performance of Schiff bases transition-metal complexes, the oxygenation constants and corresponding thermodynamic parameters ΔH° , ΔS° were measured, the catalytic epoxidation of styrene at ambient temperature were studied, and the substituents effect and macrocyclic effect of these complexes in these reactions were also discussed in this paper. The structure of the investigated transition-metal complexes ML were illustrated in **Figure 1**.

The ML^1Cl and ML^2Cl were prepared according to the literature method⁶. HL^3 and HL^4 were synthesized by the similar method: by the condensation of 5-chloro-2-hydroxybenzophenone with one amino group of 1,2-diaminobenzene and followed by the condensation of its remained free amino group with the salicylaldehyde substituted by morpholino or benzo-10-aza-15-crown-5⁷ (HL^3 : m.p. 178~180 °C, yield: 82%; HL^4 : m.p. 144~146 °C, yield: 76%). Their cobalt (II) and manganese (III) complexes were obtained from the coordination of appropriate ligand with cobalt acetate or manganese chloride

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according to the general methods (all m.p. of the Co (II) and Mn (III) complexes were above 300 °C, the yield were 71%~76%). Their structures were characterized by IR, MS, ¹H NMR and elemental analysis. The oxygenation constants and thermodynamic parameters of CoL¹~CoL⁴ presented in **Table 1** were determined by the known equipment and method⁸ (diglyme as solvent, 0.99 mol·L⁻¹ of pyridine as axial ligand (B), 5×10⁻³ mol·L⁻¹ of complexes, 9.5×10⁴ Pa of oxygen partial pressure and specific temperatures).

Figure 1 Structures of ML

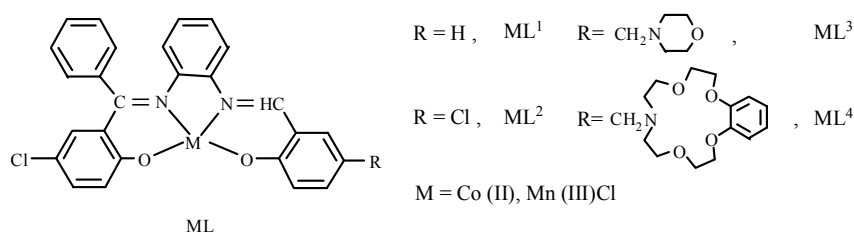


Table 1 Oxygenation constants and thermodynamic parameters ΔH^0 and ΔS^0 of CoL

Complexes	B	T(°C)	LnK _{O₂} (mm ⁻¹)	H ⁰ (KJ.mol ⁻¹)	S ⁰ (J.K ⁻¹ .mol ⁻¹)
CoL ¹	Py	-5	-4.36	-36.25 ± 0.02	-171.51 ± 0.05
		0	-4.64		
		15	-5.45		
		25	-5.94		
CoL ²	Py	-5	-3.96	-38.69 ± 0.03	-177.28 ± 0.02
		0	-4.26		
		15	-5.11		
		25	-5.62		
CoL ³	Py	-5	-3.12	-41.12 ± 0.05	-179.37 ± 0.02
		0	-3.44		
		15	-4.33		
		25	-4.83		
CoL ⁴	Py	-5	-2.32	-44.34 ± 0.03	-172.72 ± 0.03
		0	-2.65		
		15	-3.64		
		25	-4.31		

As shown in **Table 1**, the dioxygen affinities and thermodynamic parameters H^0 and S^0 were significantly influenced by the electronic property and structure of the substituents R on a salicylidene of the ligands. The electron-releasing group (R = -CH₂N) in CoL³ and CoL⁴ can increase the electron density of the center metal cation through π -conjugation system in the ligands so as to stabilize the O₂-Co (II) bond. On the contrary, the electron-withdrawing group (R = Cl) decreases the electron density of the center metal cation and makes the O₂-Co (II) bond to be formed difficultly. Whereas, with the similar electronic property to that of R substituent in CoL³, CoL⁴ showed much more increased dioxygen affinities than CoL³, it is obviously not the contribution of the electron-releasing group (-CH₂N) but the result caused by the macrocyclic effect of the azacrown ether ring. Accordingly, the order of their dioxygen affinities is CoL⁴ > CoL³ > CoL²~CoL¹. In addition it also showed that the H^0 contributed to the formation of O₂-Co (II) bond.

The species with larger oxygenation constants possess smaller H° . So their diversity can also be used to judge the dioxygen affinities of CoL.

The manganese (III) complexes as monooxygenase model were employed to catalyze the epoxidation of styrene. To a solution of bromobenzene (0.5 mmol), imidazol (0.1 mmol), styrene (0.5 mmol) and iodosylbenzene (1.0 mmol) in acetonitrile (4 mL) was added $MnLCl$ (0.01 mmol). Then the mixture was vigorously stirred for 1 hr at 20 °C. The experimental results were analyzed by GC (SE 30 column) and summarized in **Table 2**.

Table 2 Epoxidation of styrene catalyzed by the Mn(III) complexes

Complex	Conv. of styrene / %	Yield of epoxidation / %	Selectivity / %	TOF
MnL^1Cl	22.1	20.2	91.4	11.1
MnL^2Cl	30.6	28.0	91.5	15.3
MnL^3Cl	42.4	39.7	93.7	21.2
MnL^4Cl	54.9	53.1	96.9	27.5

TOF=Turnover frequency (mole styrene converted per mol catalyst per hour)

The catalytic activities of Mn (III) complexes were in the order of $MnL^4Cl > MnL^3Cl > MnL^2Cl > MnL^1Cl$. It is in accord with that of the dioxygen affinities of corresponding Co (II) complexes. An analogous principle about the effect of R structure on the catalytic epoxidation performance and the dioxygen affinities of ML seem to exist. Visibly, MnL^4Cl , which contains a pendant benzoaza crown ether on aryl ring of the ligand, is the best one among these complexes. Using MnL^4Cl , the conversion of styrene is 54.9%, which is two times more than that of MnL^1Cl . The reason may be due to the benzoaza crown ether ring can construct hydrophobic microenvironment around the coordination center and favor the formation and protection of the active species $O=Mn(V)$ by the hydrophobicity of outer ethylene groups in the mono-azacrown ether ring⁹.

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